# Influence of kaolinite/carbon black hybridization on combustion and thermal decomposition behaviors of NR composites

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Abstract: A series of NR composites filled with modified kaolinite (MK), carbon black (CB) and the hybrid filler contained MK and CB, were prepared by melt blending. The microstructure, combustion and thermal decomposition behaviors of NR composites were characterized by TEM, XRD, infrared spectroscopy, cone calorimeter test (CCT) and thermal-gravimetric analysis (TG). The results show that the filler hybridization can improve the dispensability and shape of the kaolinite sheets in the rubber matrix and change the interface bond between kaolinite particles and rubber molecules. NR-3 filled by 10phr MK and 40phr CB has the lowest heat release rate (HRR), mass loss rate (MLR), total heat release (THR), smoke production rate (SPR) and the highest char residue among all the NR composites. Therefore, the hybridization of the carbon black particles with the kaolinite particles can effectively improve the thermal stability and combustion properties of NR composites.

Keywords: kaolinite; carbon black; hybridization; Combustion behaviors; thermal stability; natural rubber.

## 1. Introduction

Polymers filled with nanolayered silicate clay particles have gained a significant research interest in the past two decades since the invention of nylon-clay based nanocomposites by Toyota R&D group

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[1-3]. They reported good improvement in mechanical, thermal and physical properties in nylon/nanoclay system and further this research extended to all other polymer material by various authors and improved properties is observed in various thermoset, thermoplastic and rubber polymers [4-6]. Thus, this nano-concept is highly relevant for rubber compounds since their application requires filler reinforcement. Rubber in particular is an important class of polymer material due to their specific applications [7]. About 70% of rubbers are used in automotive tyre and tyre based products, 10% in footwear and engineering products and about 10% in mechanical goods and remaining in other applications. In most applications [8], carbon black (CB), silica and inorganic minerals have been used as the main reinforcing fillers that increase the usefulness of rubbers. Recently, Clays have been widely used as non-black fillers in the rubber industry [9, 10]. A lot of studies have been carried out on organomodified clay rubber nanocomposites [3, 4, 10]. This involved the use of various elastomers such as natural rubber [11, 12], styrene butadiene rubber [12-14], nitrile butadiene rubber [15-17], ethylene propylene diene rubber [18, 19], chlorobutyl rubber etc. In general, literature work is focused on the preparation of rubber-nanoclay composites using solution and melt mixing, milling, radiation induced curing, latex dispersion, pre-vulcanization and two-roll mixing.

Natural rubber [20] is an important elastomer with a wide range of applications. Although NR is known to exhibit numerous outstanding properties, reinforcing fillers are necessarily added into NR in most cases in order to gain the appropriate properties for specific applications. A wide variety of particulate fillers are used in the rubber industry for various purposes, of which the most important are reinforcement, reduction in material costs and improvements in processing. Over the years montmorillonites have been used for the preparation of organomodified nanofillers. The use of kaolin in the preparation of organomodified filler for natural rubber has also been reported. Some works have been carried out in literature in natural rubber-clay composites and improved results in mechanical and thermal properties are observed. Varghese and Karger-Kocsis produced the NR based nanocomposites with 10 wt% natural and synthetic layered silicates via the latex compounding method [21]. López-Manchado et al [22] prepared the rubber compounds based on NR reinforced with octadecylamine-modified bentonite. The organoclay shifted the nanocomposite thermal decomposition to higher temperature in comparison with the neat NR. Stephen et al [11] studied the effect of microfillers on the thermal stability of natural rubber (NR), carboxylated styrene buta-diene rubber (XSBR) lattices and their 70/30 NR/XSBR blend using thermogravimetric method. Microcomposites of

XSBR were found to be thermally more stable than unfilled samples. Liu and Zhang et al. [19, 20] elaborated the influence of the compound with kaolinite and silica on properties of nature rubber composites via melt blending, and found the filler hybrid can effectively improve the thermal decomposition temperature. In addition, an exfoliated natural rubber/organo-clay nanocomposites with outstanding thermal stability was successfully prepared by direction blending in a laboratory two-roll mill [23, 24]. A kind of natural rubber composite compounded with kaolin modified with sodium salt of rubber seed oil (RSO-Na) was prepared by melt intercalation [25, 26]. Styrene butadiene rubber (SBR)/natural rubber (NR)/organo-bentonite nanocomposites [12, 27] were prepared from emulsions. The effect of organo-bentonite on the mechanical properties, thermal stability and swelling behavior was investigated. The changes in properties of calcined clay-filled NR in which the clay was partially replaced by different CB types were also referred [28]. Recently, a new biopolymer NR nanocomposite synthesized by melt blending of the clay modified with Fatty amides (FAs) from palm olein has been prepared [29]. The NR-modified clay nano-composites show higher thermal stability and significant improvement of mechanical properties in comparison with those of the pure NR.

Clay minerals can improve the strength, gas barrier and thermal properties of rubber composites due to the special layered structure. Carbon black (CB) has been extensively exploited in numerous rubber engineering products to enhance the tensile strength, tear strength, modulus and abrasion resistance. However, silica provides a unique combination of tear strength, abrasion resistance, aging resistance and adhesion properties. Each kind of filler possess their own advantages, the utilization of hybrid filler or blends of silica, CB and clay minerals in rubber should give the benefits from each filler [8]. Therefore, a series of rubber composites were prepared with natural rubber as matrix, modified kaolin and carbon black as reinforcement in this study. And, the influence of modified kaolinite and carbon black hybridization on combustion and thermal stability properties of natural rubber composites was investigated by cone calorimeter test (CCT) and thermal-gravimetric analysis (TG) [11].

# 2. Experimental

## *2.1 Materials*

The raw kaolinite was obtained from SanXing High-New Material Company of Zaozhuang, China. Its chemical compositions (mass%) are as follows: $SiO_2$, 44.68; $Al_2O_3$, 36.73; $Fe_2O_3$, 0.29; MgO, 0.62; CaO, 0.07; $Na_2O$, 0.07; $K_2O$, 0.52; $TiO_2$, 1.14. The particles size of kaolinite that smaller than 1 μm

was 90%, obtained by Malvern laser particle size analyzer. Natural rubber (NR, 3# ribbed smoked sheets) was supplied by Hainan Natural Rubber Industry Group, China. The carbon black (CB, N330) was purchased from Tianjin Dolphin Carbon Black Company, China. The fatty acid salt (Y-1) was of our own manufacture. Other materials were available commercially.

### *2.2 Preparation of natural rubber composites*

The kaolin was reacted with the modifier in water. In a typical run, the beneficiated kaolin was dispersed in water at the content of 20% and 1.5% fatty acid salt was allowed to react for one hour at around 80 °C. The modified kaolin was filtered, dried at 110 °C and ground. Then, the modified kaolinite and carbon black were blended with raw natural rubber to prepare NR composites using a two roll mill [23, 24]. The formulations of NR composites (phr) are as follows: NR, 100.00; Zinc oxide, 5.00; Stearic acid, 4.00; Accelerator M, 1.00; Antioxidant D, 1.50; Sulfur, 3.00; Filler, variable; phr is the abbreviation of mass parts per 100 mass parts rubber. The preparation procedure of rubber composite can be briefly described as following: raw rubber was plasticized in the open mill, then zinc oxide, stearic acid, accelerator, antioxidant, filler and sulfur were added into the plasticized NR in turn, and mixed even for 12~15min. The rubber mixture in the form of sheets of 150×150×2 mm was vulcanized in a mould at 153 °C in a press up to the optimum cure time. The applied pressure was 10.0 MPa. The samples were cooled rapidly in air at the end of the curing cycle.

### *2.3 Characterization*

Cone calorimeter is one of the most effective bench-scale methods that attempts to simulate real-world fire conditions, showing great important significance in the research and development of new flame-retardant materials [30]. The parameters, such as time to ignition (TTI), heat release rate(HRR), mass loss rate(MLR), effective heat of combustion(EHC), specific extinction area(SEA), smoke production rate(SPR) and total smoke production(TSP), are used to characterize the combustion behaviors of materials. The cone calorimeter (FTT, UK) tests were irradiated at a radiation heat flux of 50kW·m$^{-2}$ according to ISO 5660 standard procedures. Specimens for cone calorimeter test were 100×100×3 mm$^3$ about 35g. And, four kinds of NR composites have been carried out in the cone calorimeter test.

Thermogravimetric analysis of the samples was carried out in an Evolution 2400 (Setaram, France)

analyzer in a flowing nitrogen atmosphere. Sample was put in an alumina crucible and heated from 25 to 600 °C. And, the heating rate was set as 10 K $min^{-1}$. TEM observations of rubber composites were performed on an H-800-1 transmission electron microscope (Hitachi Co., Japan) with an acceleration voltage of 200 kV. Infrared spectroscopy analysis was carried on a Nicolet NEXUS-670 Fourier transformation infrared spectrometer. X-ray diffraction patterns were collected using a MSAL-XD2 X-ray diffractometer. Incident X-ray radiation was produced from a line focused PW3373/10 Cu X-ray tube, operating at 36kV and 30mA, with Cu Kα radiation of 1.540596Å. The incident beam passed through a 0.04 rad soller slit, a 1/2° divergence slit, a 15mm fixed mask, and a 1° fixed antiscatter slit. Scanning speed is 4°/min.

# 3. Results and discussion

## *3.1 Cone calorimeter test*

### *3.1.1 Heat release rate (HRR)*

Among many fire reaction properties, HRR is generally recognized as the most important in controlling fire hazards [31]. Fig. 1 gives the HRR curves of the NR composites as a function of time. The HRR curve of NR-1 shows a very rapid increase after ignition and reaches the maximum (2436.2 kW $m^{-2}$) at 40 s, with a total burning time of 160 s. The presence of fillers in cured NR composites significantly decreases the HRR values. With the incorporation of fillers, the HRR decreased, the combustion time increased, and the peak shape of HRR curve gradually tends to be much wider. When only contained one kind of filler, the HRR of NR-2 and NR-4 are both higher than that of NR-3 contained hybrid filler of MK and CB. In the case of NR-3, it shows a slower combustion rate giving a single HRR curve with a peak reduced to 1363.3kW$m^{-2}$, with a total burning time of 210 s. The corresponding peak HRR of NR-3 is reduced by 44.0% lower than that of NR-1. The hybridization of kaolinite and carbon black particles is very beneficial to improve the combustion performance.

**Insert figure 1 here**

The above phenomenon can be explained by the crosslinking density and the bound rubber of the NR composites, and it can be included that NR-3 has much higher crosslinking density. The kaolinite sheets finely dispersed in the rubber matrix act as the barrier to lengthen the running distance of heat

flow [20], and delay the penetration of surface heat flow into the inner of polymer matrix in combustion. The combustion of NR composites is postponed due to the barrier action of kaolinite sheets. Moreover, kaolinite sheets have large specific area about 30 $m^2/g$. Rubber molecule chains are easily absorbed on the surface of kaolinite sheets through multipoint contact due to the strong interaction of two-phase [20]. The cross-linking density of NR contained kaolinite particles becomes large. The rubber molecules were not easy to move among the kaolinite sheets. The rubber chains were trapped and changed into the bound rubber particles. The fine carbon particles are easy to form the small aggregates with a lot of pores. The voids of the aggregates are usually filled by the rubber molecules. These rubber molecules are also changed into bound rubber. The bound rubbers are helpful to form the char layer which can delay the combustion of NR composites. Therefore, the incorporation of fillers is beneficial to reduce the heat release rates of NR composites. When kaolinite hybridized with carbon black, the carbon black particles act as the role of spherical disperse medium among the kaolinite sheets, which improves the dispensability of both fillers and increases the amount of the available kaolinite sheets in the shear processing. The aggregates of carbon black particles become small and the void spaces among the particles are increased. The system with hybrid fillers becomes much stronger in restricting the movement of rubber molecule chains. Much more bound rubber particles can be obtained and change into char layers in these systems. These char layers effectively retard the surface heat to transport into the inner of the NR composites. The char layers are very beneficial to hinder the further combustion of NR composites [32]. Therefore the hybridization of kaolinite and carbon black particles is very effective in improving the combustion performance of NR composites.

*3.1.2 Mass*

Fig. 2 shows the mass of the char residues of the NR composites. The addition of fillers can increase the char residues and prolong the combustion time. It can be seen that when NR-1 is completely burnt at around60 s, the NR composites containing the filler are still not burnt for 23.9-30.0 % of their original masses. And, NR-3 has the highest char residue among all samples. The above results are correlated well with HRR results. That is, the greater the amount of char residue, the more is the decrease in HRR. The physical process of the char residue would act as a protective barrier, which can thus limit the oxygen diffusion to the substrate or low the volatilization rate [33]. NR-3 filled by hybrid

filler shows the best combustion performance.

**Insert figure 2 here**

Fig. 3 shows that NR-3 sample has a much wider peak and a lower peak value of mass loss rate curve than the pure sample (NR-1) and NR contained single filler (NR-2, NR-4). The results suggest that the hybridization of kaolinite and carbon black particles can effectively reduce the mass loss rate and retard the combustion of NR composites. The mass loss rate curve of NR-1 shows a very rapid increase after ignition and reaches the maximum (0.686g $s^{-1}$) at 42 s. With the incorporation of fillers, there are complex mass loss rate curves with dual peak as for NR-2, NR-3 and NR-4. It can be seen that the samples filled by different fillers will be decomposed in two stages. In the case of NR-2, NR-3 and NR-4, the first peak appears at 30s, 58s, 44s, respectively, and the corresponding peak value is 0.282 g/s, 0.377 g/s and 0.459g/s. The second peak appears at 46s, 80s, 58s, respectively, and the corresponding peak value is 0.401 g/s, 0.223 g/s and 0.567g/s. The second mass loss peak stands for the decomposition of the partial char layer. The appearance of the second peak is in the order of NR-2 with kaolinite, NR-4 with carbon black and NR-3 with hybrid fillers. The hindering behavior of kaolinite sheets to heat flow and rubber chains is helpful to form the retardant flame carbon layer. However, the carbon layer will be partly decomposed in the further combusting due to the big gap between the kaolinite sheets. Therefore, the decomposition phenomenon of residual char appears in the first. For NR-4, the larger amount of void spaces among the carbon black particles can restrict the motion of rubber chains and are beneficial to generate much more retardant flame carbon layer. Thus, its peak of char layer decomposition lags that of NR-2 with kaolinite particles. But its decomposition rate of char layer is much higher than that of NR-2 due to the lack of barrier function like kaolinite sheets. There is a very favorable result for the NR-3. The second mass loss peak occurs at the latest and reduces to 0.223 g/s. The data show that NR filled by the hybrid filler with kaolinite and carbon black can obtain much stable char layer in combustion. The phenomenon is attributed to the combined restriction effect of kaolinite and carbon black particles to heat flow and rubber molecule chains.

**Insert figure 3 here**

*3.1.3 Total heat release (THR)*

THR is almost independent of the external heat radiation, ventilation rate and the extent of damage of samples. It is a measurement of the internal energy of the material, to a certain extent, independent of the environmental factors [30]. The pure natural rubber (NR-1) is about 720.3kJ·$m^{-2}$ in THR. NR-2, NR-3 and NR-4 is 571.6, 599.0 and 604.4kJ·$m^{-2}$, respectively. The THR of NR composites with fillers have different degrees of reduction than NR-1 without any additives under the same conditions, which may be the fact that there is much char residue formed in the case of the sample with filler. The decreasing amplitude of THR is the largest for NR-2 only filled by kaolinite, and there is a slight increase for NR-3 and NR-4 contained carbon black. It can see that NR-2 has the lowest THR, which due to the hindering behavior of kaolinite sheets to heat flow and the char residue formed in combustion.

*3.1.4 Smoke production rate (SPR)*

The smoke consists of suspension of solid particles, liquid particles, and gaseous substances generated in the process of pyrolysis or combustion. Therefore, smoke production rate is also an important parameter to evaluate the flame retardancy. The bigger the SPR is, the worse the flame retardancy of the materials is [34].

**Insert table 1 here**

Fig. 4 shows the SPR curves of NR composites at the heat flux intensity of 50kW$m^{-2}$. The SPR peak of NR-1 (0.781$m^2$·$s^{-1}$) is the largest one of all the samples. It can be seen that fillers can significantly suppress the SPR of NR composites. The SPR of NR-2 and NR-3 reduces to 0.442$m^2$·$s^{-1}$ at 46s and 0.491$m^2$·$s^{-1}$ at 49s. The NR-4 curve appears two peaks at 46s and 56s, and the SPR is 514$m^2$·$s^{-1}$ and 714$m^2$·$s^{-1}$. In addition, the SPR peak of NR contained kaolinite particles become much lower and wider. It also indicates that the hindering behavior of kaolinite sheets is beneficial to form the stable char layer, and the carbon layer is easy to be decomposed in combustion for the NR-4 only filled by carbon black particles. The total smoke production (TSP) can be obtained by integrating the SPR curves. The higher the TSP is, more incomplete the combustion, and the better the flame retardancy of the materials is. Table 1 shows the TSP of NR composites at the heat flux intensity of 50kW· $m^{-2}$. NR-3 with 10MK and 40CB has the highest TSP up to 22.28. The result suggests that NR-3 has been

endowed with the best flame-retardant performance due to the hybridization of flaky kaolinite particles and spherical carbon black particles.

**Insert figure 4 here**

*3.1.5 Carbon dioxide*

When the pure natural rubber is exposed to heat radiation source in short time, intense burning will lead to generating a large amount of smoke. When NR filled by the filler, burning rate and smoke production was relatively reduced due to the inhibition of char layer to the combustion. Fig. 5 shows the $CO_2$ curves of NR composites at the heat flux intensity of 50kWm$^{-2}$. For NR-2 with 50MK, there is not peak in the $CO_2$ curve. For the NR-4 with 50CB and NR-3 with 10MK+40CB, carbon dioxide release peaks are postponed than that of pure NR, and a trough emerges at 60s and 80s respectively. It shows that the burning behavior of NR-2 is very temperate and single in presence of kaolinite sheets, and the combustion of NR-3 and NR-4 become more complex than that of NR-2 due to the incorporation of carbon black particle in material system. For the NR-3 and NR-4, the peak in $CO_2$ curves indicates the decomposition of surface char layer, and the trough represents the forming of second char layer. The span time from the peak to the trough can illustrate the difficulty degree of the second char layer to decompose. The longer the time is, the more difficult the decomposition of carbon layer is. For the NR-4, the span time is 31s, and that of NR-3 is 58s. It is obvious that the second carbon layer of NR-3 is more compact and stable in combustion process than that of NR-4. The composite with 10MK+40CB has better flame retardant properties. The phenomenon can be explained by the hybridization of kaolinite and carbon black.

**Insert figure 5 here**

*3.1.6 Carbon monoxide*

Carbon monoxide (CO) is the product of polymer in combustion process. The larger the quantity is, the more incomplete the combustion of materials is. Fig. 6 shows the CO curves of NR composites at the heat flux intensity of 50kWm$^{-2}$. Release amount of CO for pure NR (NR-1) is the largest among all samples. The intense burning happens in a very short period of time and results in the insufficient

combustion. Therefore, the corresponding CO amount of pure rubber (NR-1) increases markedly in combustion, and the releasing peak of $CO_2$ and CO are located in the front of the filled composites. The CO release curve of 50MK filled composites is monotonous, and the release quantity is very low, which indicates that the composite only filled by MK is difficult to form the dense flame retardant carbon layer and the combustion is more complete than NR-3 and NR-4. For the composites filled with CB, the CO release curve of the composite with 10MK+40CB (NR-3) is more complex and appears several lagging peaks. The CO quantity is higher than that of the single CB filled composite (NR-4). The phenomenon suggests that the hybridization of CB and MK can prompt the forming of dense char layer and NR-3 shows more complex decomposition behavior.

**Insert figure 6 here**

## *3.2 Thermogravimetric analysis (TG)*

### *3.2.1 Thermal stability of kaolinite and carbon black*

The thermal behavior of kaolinite was studied in numerous papers and the results from the thermal analysis of our kaolinite were similar to those reported in the literature [35]. On the TG curve of kaolinite, the mass losses by 0.20% and 11.08% are observed in the temperature intervals of 40-109°C and 363-600°C, respectively (Fig. 7a). These mass losses correspond to the DTG and DSC peaks centred at 62°C and 507°C, respectively. The former is attributed to the removal of the surface adsorbed water (moisture) and the latter is represented to the dehydroxylation process with formation of metakaolinite [36]. The final mass loss is 11.35% for this kaolinite. On the TG curve of CB, the mass losses by 1.64% are observed in the temperature intervals of 20-600°C (Fig. 7b). The few mass loss is attributed to the removal of the surface adsorbed water (moisture) and the dehydroxylation process of phenolic hydroxyl and carboxy hydroxyl on the surface of carbon black particles.

**Insert figure 7 here**

### *3.2.2 Thermal stability of natural rubber composites*

TG is a commonly employed approach to evaluate the thermal stability and thermal decomposition behavior at various temperatures by measuring the degradation temperature at which

different mass loss occurs, the maximum decomposition rate ($R_{max}$), the residue mass of rubber composite ($M_R$) and the residual char mass ($M_C$) [33].

**Insert table 2 here**

Fig. 8 shows the TG and DTG curves respectively of NR-1 to NR-4, and table 2 is the result of the degradation temperature at which different mass loss occurs and the residual mass of rubber composites. Compared to the pure natural rubber (NR-1), $R_{max}$ of NR composites was significantly reduced due to the incorporation of fillers. $T_5$ of NR-2 with 50phr MK, NR-3 with 10phr MK+40phr CB and NR-4 with 50phr CB was 237°C, 264, 252°C and increased by 31°C, 58 and 46°C, respectively. $T_{50}$ of NR-2, NR-3 and NR-4 also increased by 19°C, 22°C and 20°C. $T_{10}$ and $T_{30}$ show the same change tendency as like the $T_5$ and $T_{50}$. The decomposition temperature at which different mass loss occurs for NR-3 is the highest among four samples. NR composite with 10phr MK+40phr CB was endowed the best thermal stability compared to others.

**Insert figure 8 here**

**Insert table 3 here**

Based on the formulation of NR composites, for the NR filled by 50 phr filler, the mass fraction of filler is about 30.40% in compound, the residual kaolinite mass ($M_K$) at 600°C is 30.40% × (1-11.65%) = 26.85%, the residual CB mass ($M_{CB}$) at 600°C is 30.40% × (1-1.64%) = 29.90%, and the residual mass of the compound with 10MK+40CB at 600°C is the sum of 26.85% × 0.2 and 29.90% × 0.8. The residual char mass ($M_C$) for the NR composites at 600°C can obtained by $M_R$ subtracting $M_K$ and $M_{CB}$. The residual char results of NR composites with different fillers were listed in Table 3. $M_C$ of NR-3 filled by 10phr MK+40phr CB is 5.23%, which is the highest among the four rubber samples. The residual char layer can act as an insulation material to hinder the heat flow transport into the inner of polymer matrix and is very beneficial to improve the thermal stability of NR composites. Therefore, NR-3 with 10MK+40CB is difficult to decompose in high temperature and has the highest thermal stability among all the samples.

The thermal analysis data indicate that the filler hybridization can effectively improve the thermal stability of NR composites. The results are consistent with that of the cone calorimeter test. The reason

for this improvement of thermal stability for the selected composites is resulted from the carbon black particles playing the role of spherical disperse medium and the occlusion of the fillers to the rubber chains. When the rubber filled by MK and CB simultaneously, the spherical carbon black particles acted as the role of ball among the kaolinite sheets, which improved the dispensability of both fillers and increased the amount of the available kaolinite sheets in the shear processing. The aggregates of carbon black particles became small and the void space among the particles increased. The kaolinite sheets are impermeable and can hinder the heat to transport into the inner of the NR composites [20]. In addition, in the help of the obstruction function of kaolinite sheets, the large amount of rubber chains occlude in the void spaces among the fine carbon black particles can be changed into the stable char layer at high temperature. These char layers are very beneficial to improve the thermal stability of NR composites [37, 38]. Therefore, the hybridization of kaolinite and carbon black particles is very effective in improving the thermal stability of NR composites.

### *3.3 Transmission electron microscopy analysis*

Fig. 9-a shows the transmission electron microscope (TEM) photograph of NR-2 with 50 phr modified kaolinite loadings prepared by melt blending. It can be seen that the kaolinite sheets are aligned in parallel in the NR matrix. Fig. 9-b shows TEM photograph of NR-3 filled by the hybrid fillers with 10phr MK and 40phrCB. The photograph indicates that the kaolinite sheets are dispersed disorderedly in rubber matrix and covered by the fine carbon black particles. In NR-3 with the hybrid filler of MK and CB, the particle size of kaolinite is decreased and the interface becomes more indistinct than in the NR-2 only with MK (Fig. 9-a). It is because that the bigger kaolinite particles were disaggregated into the smaller particles and the spherical carbon black particles acted as the role of disperse medium among the kaolinite sheets, which improved the dispensability of the kaolinite sheets in the processing of the compounds [39]. The hybridization of the fine carbon black particles with the kaolinite particles can obtain much better interface bond between the rubber matrix and the filler particles [20] and was benefit to improve the thermal stability and combustion properties of the rubber composites.

**Insert figure 9 here**

### *3.4 Infrared spectroscopy analysis*

Fig. 10 shows the infrared absorption spectra of NR composites with different fillers. The stretching vibration bands [40] of hydroxyl (OH) at 3696 $cm^{-1}$, 3652$cm^{-1}$ and 3621$cm^{-1}$ are very strong in the NR-2 with 50phr kaolinite whereas the corresponding band are disappeared in NR-3 with 10phr MK and 40phr CB. The disappearance of OH absorption band should be related to the random dispersing of kaolinite sheets and the coating of carbon black particles on kaolinite sheets. When kaolinite hybridizes with carbon black, the kaolinite sheets are dispersed efficiently and distribute in disordered orientation in rubber matrix. The spherical carbon black particles act as the role of ball among the kaolinite sheets and play an important role in improving the dispensability of the kaolinite sheets. The disordered orientation leads to the disappearance of the OH absorption band of kaolinite.

**Insert figure 10 here**

The band at 3035 $cm^{-1}$ attributing to =C-H vibrations of isoprene in NR composites contained fillers (50MK, 10MK+40CB, 50CB) becomes weak compared to that in pure NR. The wavenumbers of =C-H vibrations in NR-2 and NR-3 shift to 3042 $cm^{-1}$ from 3035 $cm^{-1}$. In addition, there were some significant changes in the region from 2960 to 2850 $cm^{-1}$ attributing to –C-H wagging vibration of isoprene. In NR-3 sample, the bands at 2918 $cm^{-1}$ and 2850 $cm^{-1}$ become more intense whereas the band at 2958 $cm^{-1}$ is reduced obviously. It can be seen that the interaction intensity between surfactant molecules on the filler surface and rubber molecules has been changed due to the hybridization of modified kaolinite and carbon black. For the pure NR sample, the band at 1662-1397 $cm^{-1}$ is related to the stretching vibration of C=C bond of isoprene. These absorption bands show the significant changes in the shape and intensity, especially for the NR-3 contained with the hybrid filler of kaolinite and carbon black. Besides, a new band occurs at 1431 $cm^{-1}$ attributing to C=C stretching vibration in NR-4. It can be seen that there is interaction between carbon black particles and rubber molecules. The region [36] from 1088 $cm^{-1}$ to 1009 $cm^{-1}$ is the absorption band of Si-O stretching vibrations, and 915 $cm^{-1}$ belongs to the bend vibration band of inner surface OH. The intensity of these bands at 1088-1009 $cm^{-1}$ and 915 $cm^{-1}$ decreases in NR-3, which maybe results from the decrease of kaolinite content. The bands at 834 $cm^{-1}$ belonging to the bend vibration of =C-H are enhanced with the increasing of CB content, on the contrary, the bands of 745 $cm^{-1}$ attributing to C-H bend vibration of $CH_2$ are reduced. The corresponding wavenumbers have a little shift in NR-3 compared that in NR-2 and NR-4. It indicates

that the chemical environment of these groups has been modified due to the hybridization of fillers. The hybridization is beneficial to improve the dispensability of fillers and the interaction between the fillers and rubber matrix. The improvement can further enhance the thermal stability and retardant combustion properties.

### *3.5 X-ray diffraction analysis*

**Insert figure 11 here**

The basal spacing of (001) and (002) are respectively $7.214\times10^{-1}$ nm and $3.587\times10^{-1}$ nm, showing the characteristic peaks of kaolinite. In general, the kaolinite peaks between (001) and (002) in X-ray diffraction analysis will not appear when the samples are characterized by the means of oriented preparation, the kaolinite sheets are aligned in parallel [19, 20]. On the contrary, these peaks will emerge clearly at the corresponding location when the samples are characterized by powder diffraction, and the kaolinite sheets are in disordered distribution. Fig. 11 shows the results of X-ray diffraction of natural rubbers filled with modified kaolinite and carbon black. Compared to NR-2, there is a little fall in intensity for the (001) and (002) peaks in NR-3. When NR-2 is filled by 50phr modified kaolinite, there are no any peaks appear at the region from (001) and (002) in XRD pattern. It can be seen that kaolinite sheets should be distributed in parallel and orientated alignment in NR-2 (Fig.9-a). With the decreasing of kaolinite and the incorporation of carbon black, the kaolinite sheets are dispersed completely because the carbon black particles act as a role of dispersant ball in shear processing. The kaolinite sheets are disaggregated and distributed disorderedly in rubber matrix (Fig.9-b). Then, the diffraction peaks of kaolinite between (001) and (002) begin to emerge in XRD pattern of NR-3. In addition, at the region of 35° to 40° (2θ), a peak of kaolinite diffraction becomes intense due to the disordered dispersing and other peaks are reduced in intensity in relation to the decreasing of kaolinite content. The kaolinite sheets show the special parallel arrangements in NR-2 and disperse disorderedly in NR-3, which is consistent with the dispersed pattern (Fig. 9) observed by the TEM technique. The XRD results also indicate that the dispersibility of kaolinite sheets can be improved by hybridizing with carbon black particles. The kaolinite sheets are further disaggregated and distributed randomly in rubber matrix which is very beneficial to improve the thermal stability and combustion properties of rubber composites. Therefore, NR-3 filled by the hybrid filler of 10phr MK and 40phr CB is endowed

with better thermal stability and combustion properties compared to NR-1, NR-2 and NR-4.

## 4. Conclusions

NR composites filled with different fillers, such as modified kaolinite (MK), carbon black (CB) and the hybrid fillers contained MK and CB, were prepared by melt blending. The analysis of TEM, XRD and infrared spectroscopy shows that the hybridization can improve the dispensability and shape of the kaolinite sheets in the rubber matrix and change the interface bond between kaolinite particles and rubber molecules. Cone calorimeter test and thermogravimetric analysis (TG) indicate that NR-3 has lower heat release rate (HRR), mass loss rate (MLR) and smoke production rate (SPR), higher total smoke production (TSP) and generates much more retardant flame carbon layer. NR-3 has been endowed with the best flame-retardant performance and thermal stability due to the hybridization of flaky kaolinite particles and spherical carbon black particles.

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